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Sustainable fuel for the transportation sector

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A hybrid hydrogen-carbon (H₂CAR) process for the production of liquid hydrocarbon fuels is proposed wherein biomass is the carbon source and hydrogen is supplied from carbon-free energy. To implement this concept, a process has been designed to co-feed a biomass gasifier with H₂ and CO₂ recycled from the H₂-CO to liquid conversion reactor. Modeling of this biomass to liquids process has identified several major advantages of the H₂CAR process. (i) The land area needed to grow the biomass is <40% of that needed by other routes that solely use biomass to support the entire transportation sector. (ii) Whereas the literature estimates known processes to be able to produce ≈30% of the United States transportation fuel from the annual biomass of 1.366 billion tons, the H₂CAR process shows the potential to supply the entire United States transportation sector from that quantity of biomass. (iii) The synthesized liquid provides H₂ storage in an open loop system. (iv) Reduction to practice of the H₂CAR route has the potential to provide the transportation sector for the foreseeable future, using the existing infrastructure. The rationale of using H₂ in the H₂CAR process is explained by the significantly higher annualized average solar energy conversion efficiency for hydrogen generation versus that for biomass growth. For coal to liquids, the advantage of H₂CAR is that there is no additional CO₂ release to the atmosphere due to the replacement of petroleum with coal, thus eliminating the need to sequester CO₂.

biofuels | coal | hydrogen | oil

The transportation sector relies almost exclusively on liquid hydrocarbons as the energy source. One reason cars, trucks, buses, trains, airplanes, etc. prefer to use liquid hydrocarbons is their high volumetric energy density and convenience of use. However, combustion of liquid hydrocarbon fuels leads to emission of massive quantities of CO₂ with the associated greenhouse effect. In the United States alone, oil consumption in the transportation sector approaches 13.8 million barrels per day (Mbb/d) (1), corresponding to a release of 0.53 gigatons of carbon per year (GtC/yr) (2). The current global release of carbon from all of the fossil fuel usage is estimated to be at 7 GtC/yr, and the business-as-usual scenario is expected to raise it to ≈14 GtC/yr by 2050 (3–5). The concern over increased carbon release has led to the consideration for the use of alternative carbon-free energy carriers by the transportation sector.

Some of the alternative energy carriers considered for transportation are electricity and hydrogen (6, 7). Both of these energy carriers, when produced from a carbon-free primary energy source such as nuclear, solar, wind, etc. or a renewable source such as biomass, have a potential to eliminate net carbon emission by the transportation sector. However, use of either of these carriers is laden with technical and economical challenges. For the transportation sector, probably the biggest challenge is the storage density of the energy (6). The current energy density of commercial batteries is <175 Wh/kg of battery (8). At a storage pressure of 680 atm (1 atm = 101.3 kPa), the lower heating value (LHV) of H₂ is ≈1.32 kWh/liter. In contrast, the corresponding energy density for gasoline is 8.88 kWh/liter. For a given on-board storage space, the lower storage energy densities of batteries and H₂ severely limit the driving distance (9). Furthermore, energy and cost associated with the delivery of a low-energy density carrier to an automobile is a large fraction of the overall energy and cost (6). Therefore, the

convenience of the use of a liquid hydrocarbon fuel through the existing infrastructure is a big deterrent to replacement by batteries or H₂.

Other historical reasons for the use of liquid hydrocarbon fuels have been easy access to primary resources and relatively low cost. However, the recent rise in the petroleum price has refocused the world's attention to the finiteness of this source of energy. By varying accounts, conventional oil production is predicted to peak in as little as the next 10 years to as high as 50 years (10, 11). A large number of developed, as well as developing, nations import oil for the transportation sector to support their economic activities. The looming possibility of the decline in the availability of oil is forcing the nations to consider alternate energy sources such as biomass and coal to supply liquid hydrocarbons for transportation. The use of each of these energy sources brings additional challenges.

The nations rich in coal reserves are actively exploring the option of converting coal to liquid fuels. However, the thermal efficiency of an actual Fischer-Tropsch (FT) process to convert coal to synthetic hydrocarbon liquids is <50% (12). Per unit of transportation energy consumed, the use of coal leads to added carbon release to the atmosphere. For example, about 3 kg of carbon per gallon of gasoline used is released, whereas 6–7 kg of total carbon is estimated to be released with the use of a gallon of synthetic liquid fuel derived from coal. This increase in carbon release has led to intense research for the so-called clean-coal technologies whereby carbon dioxide from the coal-to-liquid conversion process will be captured and then sequestered (13, 14).

Service points to the potential dangers associated with the sequestration of CO₂ in depleted oil/gas reservoirs, unmineable coal beds, and deep saline aquifers (15). If CO₂ leaks out, it can lead to leaching of dangerous trace elements in freshwater aquifers due to lowering of the pH and can impact soil chemistry. Clearly, massive quantities of CO₂ would be sequestered during a century's-long production of liquid fuels from coal. This would place extreme demands on CO₂ capture, storage, and monitoring systems. An alternative route whereby liquid fuels from coal can be produced without any CO₂ sequestration, as well as with no additional CO₂ emission (as compared with petroleum use), would be highly desirable.

Biomass is another energy source that has increasingly drawn attention as a source of liquid hydrocarbon fuels (16, 17). It can also be a solution to the problem of CO₂ emission from the transpor-

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Conflict of interest statement: R.A. and N.R.S. are the co-inventors of the H₂CAR process, which is trademarked by Purdue University and covered under provisional U.S. patent application 60/843678.

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Abbreviations: GtC, gigatons of carbon; H₂CAR, hybrid hydrogen-carbon; FT, Fischer-Tropsch; LDVs, light-duty vehicles; LHV, lower heating value; Mbb/d, million barrels per day; NRC, National Research Council; PHEVs, plug-in hybrid electric vehicles; PV, photovoltaic; WGS, water-gas shift.

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Table 1. Production of 13.8 Mbbl/d of synthetic oil by using biomass

Case	Gasifier efficiency, %	Biomass land area, million km ²	Required H ₂ , billion kg/yr	H ₂ land area, thousand km ²	Carbon efficiency, %	Energy efficiency, %
Conventional-I	50	5.30	0	0	26.2	29
Conventional-II	70	2.51	0	0	36.7	40.6
H ₂ CAR-I	50	1.41	276	62	≈100	52.7
H ₂ CAR-II	70	0.92	239	54	≈100	58

conventional gasifiers, the gas composition of gaseous effluent stream is found to be close to thermodynamic equilibrium (21, 22). Similarly, for the proposed gasifier, we expect CO₂ concentration to be determined by equilibrium considerations at the high temperatures of 800–1,300°C prevalent in the gasifier. Therefore, the formation of CO₂ in the presence of added H₂ will be greatly reduced. As a result, CO₂ acts as an inert that is simply circulated through the overall process. For simplicity, we have named the hybrid H₂-carbon process of Fig. 2 as the H₂CAR process.

In the H₂CAR process, addition of sufficient quantity of H₂ along with oxygen to the gasifier may be thought of as providing energy for the gasification of the biomass or coal to CO. The oxidation of H₂ is an exothermic reaction, and conversion of some H₂ to water results in the net contribution of energy needed for gasification. Alternatively, high-temperature heat from a nuclear reactor or solar concentrators can be used to supply energy for the gasification.

The advantage of feeding H₂ from a carbon-free energy source and recycling CO₂ to the high-temperature gasification step is that it decouples the reverse WGS reaction requirement from the catalyst in H₂-CO to liquid conversion reactor. Generally, the H₂-CO to liquid conversion reactors operate at temperatures below 350°C, where the reverse WGS reaction is not favorable. The H₂CAR process takes the advantage of the preferable high temperature range prevalent in the gasifier to run reverse WGS reaction. This allows a degree of freedom to tailor the FT synthesis catalyst specifically for the desired liquid hydrocarbon molecule. Another advantage of this process configuration is that net CO₂ formation is minimized. Therefore, the cost associated with CO₂ handling is reduced.

To quantify the impact of the proposed H₂CAR route, we have done order of magnitude calculations for both biomass and coal as the carbon source. In the year 2005, the United States transportation sector alone consumed nearly 13.8 Mbbl/d of the world's total oil consumption of 82.5 Mbbl/d (10). Therefore, calculations were done to displace 13.8 Mbbl/d of oil with a synthetic fuel such as diesel. It is believed that the magnitude of the United States transportation sector is large enough to provide clear insight into the pros and cons of the proposed pathway. H₂CAR results for biomass are presented first followed by those for coal.

Biomass to Liquid Fuels

Initial calculations for biomass were done for the two biocrop cases described in the NRC report (6). In case I, the “current scenario” of the NRC report, the biomass was presumed to grow at a rate of 1 kg of dry biomass/m²/yr (corresponding to 4 ton/acre/yr) with a carbon content of 0.425 kg of C/kg of dry biomass. The gasifier efficiency is 50% (based on LHV). For case II, the “future scenario” of the NRC report, the biomass growth rate was 1.5 times the current growth rate, and the gasifier efficiency was 70%. In our calculations for the conventional process, we assumed 100% conversion and selectivity in the FT reactor to the desired diesel (C₁₅H₃₂) fuel molecules. This provides an optimistic scenario for the biomass requirement and land area needed to grow the biomass. For the H₂CAR process of Fig. 2, conversion in the FT reactor was taken to be 90% with 100% selectivity to diesel fuel molecules, and the unconverted

reactants, along with CO₂, were recycled to the gasifier. ASPEN (23) simulations were done for all of the cases, and the results are summarized in Table 1. Both of the conventional cases use 15% of the biomass to dry the rest of the biomass (6), whereas in the H₂CAR processes, this drying energy is provided through combustion of additional H₂. This increases the H₂ requirement for the proposed cases but requires less land area to grow the biomass. In Table 1, H₂ is produced from solar energy, and the required land area for H₂ was calculated by using the conversion efficiency from solar to H₂ of 8.5% (based on LHV of H₂). The energy efficiencies in Table 1 are based on the energy content of biomass and H₂ arriving at the plant. The relevant results for biomass are the following. (i) The estimated land areas for both the conventional processes are too large. Even with the anticipated advancements, the land area for the conventional-II case is 27.5% of the total United States land area. This land area is greater than the current United States cropland area. (ii) The land area requirements for the proposed processes, especially for the H₂CAR-II case, are substantially lower and have a potential to be manageable. (iii) The carbon efficiency for the conventional biomass process is quite low. Nearly two-thirds of the carbon contained in the biomass is lost as CO₂. (iv) The addition of H₂ in the H₂CAR process improved the overall efficiency of the process. (v) Another associated benefit of H₂CAR process is that diversity of crops can be maintained because any type of biomass can be gasified, and Tilman *et al.* (24) have shown that plant diversity enhances the biomass yield by 180% over monocultures. Also, a diverse biomass growth has a better chance of survival in droughts. (vi) The ability to use diverse biomass also provides an additional degree of freedom to tailor biomass growth for the maximization of carbon pickup from the atmosphere without the constraints of relative quantities of lignin, cellulose, hemicellulose, starch, oil, sugar, etc. in a plant. (vii) Land area radius decreases to support a given size of plant. (viii) Less space is required for storage of biomass. (ix) Less fertilizers and pesticides would be required for the same quantity of liquid fuel production, if any. (x) There would be less wear and tear to the land. (xi) Less biomass demand to produce same quantity of transportation fuel implies less energy and water input to grow the required amount of biomass.

Even though the amount of H₂ needed is large, the land area needed to produce it by using solar energy is a small fraction of the land area to grow the biomass. However, the intermittent nature of the H₂ from solar energy will have strong repercussions on how the biomass gasifier will be operated and will require further innovations. H₂ from nuclear reactors will not face this challenge because H₂ will be available at a steady production rate around the clock. For this reason, it is likely that initial H₂CAR plants may be built by using H₂ from nuclear reactors.

It should be emphasized that the proposed “sun to wheels” solution is successful in providing a viable sustainable route to meet the hydrocarbon fuel need for the total United States transportation sector. The interesting aspect is that it does so with a reasonable land-area requirement. The potential attractiveness of our proposal will improve with further advancements in the production, distribution, and end-use technologies.

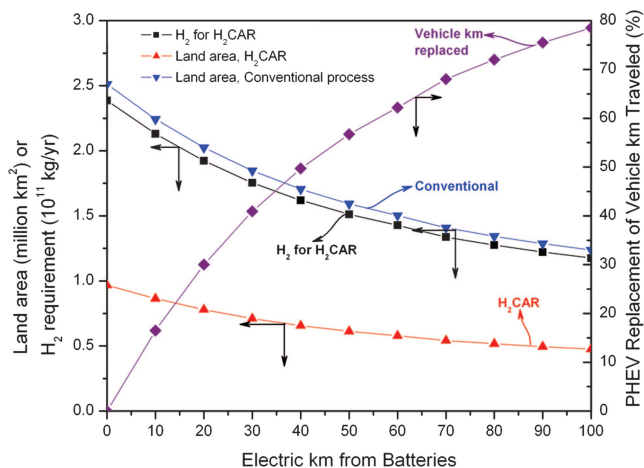


Fig. 5. Land-area and H₂ requirement for conventional and H₂CAR process using PHEVs as a function of drivable distance traveled per single full charge of batteries.

With the added verification in the estimated production from the conventional gasification route, we estimate that from 1.366 trillion kg of dry biomass/yr, the H₂CAR process can produce liquid fuels for 99.6% of the United States transportation sector. This is indeed a remarkable result for the proposed “sun to wheels” H₂CAR process that takes us closer to meeting the needs of the entire United States transportation sector.

Effect of Improvement in Other Technologies

Currently, light-duty vehicles (LDVs) consume 8.9 Mbbbl/d of the 13.8 Mbbbl/d used by the entire United States transportation sector. If all of the LDVs were to be replaced with gasoline hybrid electric vehicles (GHEVs), then the demand for gasoline would decrease, resulting in reduced biomass demand. Assuming that GHEVs are 1.45 times more fuel-efficient than nonhybrid gasoline vehicles (6), the daily United States gasoline demand would decrease from 8.9 to 6.2 Mbbbl/d. This means that the amount of biomass needed to meet the needs of the United States transportation sector would be reduced to nearly 1.1 trillion kg per yr.

However, in the current scenario, an overall better picture emerges with the use of plug-in hybrid electric vehicles (PHEVs). Rechargeable batteries provide short-range driving capability to PHEVs. The long-range driving still depends on liquid fuels. If LDVs were replaced with PHEVs, then electricity from a PV grid could be directly used to charge the vehicles. Unlike the usual wisdom of charging the PHEVs at night by using electricity from grid, now they would be charged during the day by using solar energy. There are two immediate benefits. One is that the batteries in millions of automobiles become a very large amount of storage for solar energy. The second is that reduction in the amount of liquid fuel results in the reduced biomass and H_2 requirement for the H_2 CAR process. Fig. 5 shows some pertinent results based on Argonne National Laboratory estimates of the relationship between the range of batteries in kilometers and the vehicle kilometers traveled that could be replaced with the electric kilometer

capability of PHEVs. Thus, if all LDVs were replaced with PHEVs containing batteries that can provide driving distance of 48 km between two successive charges, then nearly 56% of total distance driven by LDVs in the United States could be powered by batteries. Only 44% of the total driven distance would require liquid fuel. Therefore, the demand for liquid fuel for the LDVs would decrease from ≈ 8.9 to 3.9 Mbb/d. Even with 1.5 kg/m²/yr biomass growth rate, only 6.4% of the United States land area will be needed with H₂ consumption, decreasing from nearly 239 billion kg/yr to 149 billion kg/yr. For the overall sustainable energy scenario, it will clearly be better to use PHEVs with the capability for reasonable driving distance by using rechargeable batteries.

Because the H_2 CAR process in conjunction with GHEVs and/or PHEVs leads to a large reduction in the amount of biomass required, one can envision a scenario where more biomass is available than is needed for the transportation sector alone. In such a scenario, a strong potential exists for supply of synthetic biofuel to other energy sectors such as residential and commercial, effectively extending the capability for storing solar energy for use around the clock. This also presents an intriguing possibility of the United States becoming a net exporter of oil.

One of the drawbacks of the H_2CAR process as described is that H_2 generation from solar is a two-step process, which cuts the conversion efficiency to nearly half of the PV efficiency (Fig. 4). Of course, one could improve the process by devising a more efficient, direct one-step solar-to- H_2 process.

Clearly, the H_2 CAR process provides an exciting possibility to supply sustainable liquid fuel for the much needed transportation sector with manageable land area. Now we will briefly explore its beneficial extension for coal-to-liquid processes.

Coal to Liquid Fuels

Unlike biomass gasifiers, coal gasifiers are much more advanced. FT processes in conjunction with WGS reaction to convert synthesis gas (syngas) to diesel are also fairly well developed. Therefore, it is relatively easy to assess the benefit of the H_2 CAR process in the context of coal to liquid fuel. For calculations with coal as the carbon source, we used the coal and the associated gasifier data available in the NRC report (6). The NRC's "current case" with gasifier efficiency of 75% was considered. Other assumptions were similar to those described for the biomass cases, and the results are summarized in Table 2.

Several observations can be made from these simulations. (i) For the conventional process, the amount of coal needed is greater than the current rate of 1.128 trillion kg/yr of coal consumption in the United States and will have a huge impact on the coal reserves. (ii) Additional CO_2 , >3 trillion kg/yr, will be emitted. If not sequestered, this corresponds to additional contribution of >0.9 GtC/yr to the current global release of 7 GtC/yr from fossil fuels. (iii) The proposed H_2CAR process is thermodynamically feasible and reduces the coal requirement to $\approx 40\%$ of that of the conventional process. There is no associated additional CO_2 release to the atmosphere. (iv) United States coal is expected to last for 244 years if used at the current consumption rate. However, if coal is used to produce liquid fuels by conventional process, this coal will last for ≈ 89 years. The use of the H_2CAR process to make liquid fuels will increase the life of coal to 144 years. (v) For the proposed process to be adopted, huge quantities of H_2 from carbon-free energy

Table 2. Production of 13.8 million bbl/d of synthetic oil by using coal with 75% gasifier efficiency

Case	Amount of coal, trillion kg/yr	Required H ₂ , billion kg/yr	CO ₂ sequestered, GtC/yr	Carbon efficiency, %	Energy efficiency, %
Conventional	1.97	—	0.9	39.9	50.7
H ₂ CAR	0.79	211	0	≈ 100	65.2

sources will be needed. It is no surprise that for the H₂CAR process, the heat content (LHV) of the H₂ used is 1.2 times the corresponding value of the coal fed to the gasifier. Energy in the H₂ goes toward producing 1.5 times more liquid product for the same amount of coal. (vi) Although the energy needed to produce H₂ is large, as discussed for the biomass case, the land area to produce it by using solar energy is quite manageable. Alternatively, H₂ could also be produced by using nuclear energy. (vii) The amount of synthetic oil produced contains ≈ 105.4 billion kg of H₂/yr. This is nearly half of the H₂ required by the H₂CAR process. If we think of the synthetic oil as a medium for storing H₂, then the large quantities of H₂ stored in the high energy density fuel by H₂CAR will solve the grand challenge problem of H₂ storage associated with the H₂ economy (6). (viii) Even under the best FT reaction conditions, $\approx 27\%$ of the energy contained in the final liquid fuel product is liberated as thermal energy rather than being stored as fuel. This coproduction of thermal energy has a large negative impact on the H₂ demand for the H₂CAR process. There is clearly a need for better alternate chemical pathways that can use energy from carbon-free sources in conjunction with carbon moieties contained in coal to efficiently produce synthetic liquid for the transportation sector. (ix) Another advantage of the H₂CAR process is the decreased annual rate of release of pollutants like Hg. (x) The overall energy efficiency of the H₂CAR process based on the energy content of coal and H₂ is $\approx 65\%$ and is higher than the conventional process's energy efficiency of nearly 51%. Similar to the biomass cases in Table 1, we find that the H₂CAR-based processes have higher efficiency.

Conclusions

In summary, the proposed hydrogen-carbon economy and associated H₂CAR process provide compelling alternatives. The primary function of biomass or coal is envisioned to provide carbon atoms for the much-needed hydrocarbon liquid to propel the transport sector. The required H₂ for the hydrogenation process is supplied by carbon-free energy sources such as solar, nuclear, wind, etc. To preserve the carbon atoms, the energy need for the transformation process is also supplied from the alternate source. In some cases, this energy need could be met through the combustion of additional H₂. A big advantage is that, with recycle to the gasifier, there is no additional CO₂ released to the atmosphere due to the replacement of petroleum with coal. Probably the greatest benefit is achieved with the use of

biomass as the carbon source. This approach has the potential to provide a sustainable route to transportation fuel with much lower land area than hitherto seen for the cultivation of the bioenergy crop. The reduction to practice of this route could provide the transportation sector with a high density liquid energy source for the foreseeable future of the human race without a net CO₂ emission to the environment. A final and very important advantage of H₂CAR is that it uses the existing fuel distribution infrastructure.

The proposed H₂CAR-based processes also have a strong impact on the future areas of research. The primary research emphasis needs to be on cost-effective H₂ production from a carbon-free energy source such as solar or nuclear. In addition, efficient, low-cost, and easy-to-operate methods are needed for the conversion of biomass through reaction with H₂ to a suitable hydrocarbon liquid fuel. In the short term, the same is true for the conversion of coal to liquid. The current conversion route of gasification followed by a H₂-CO liquid conversion reaction is quite inefficient, and an alternative efficient hydrogenation process is highly desirable. In the mean time, until such alternate processes are discovered, the preservation of carbon atoms in the current gasification and H₂-CO liquid conversion reaction is essential. A proposed solution in this work is to co-feed H₂ and recycle CO₂ from the H₂-CO liquid conversion reactor to the gasifier. Feasibility and development of such gasifiers especially for biomass will require extensive research. Needless to say, if we are going to continue with the current transportation fuel infrastructure, the efficiency improvement in the internal combustion engine will be highly beneficial. Clearly, the proposed concepts deemphasize research in CO₂ sequestration as well as on-board H₂ storage. The synthesized liquid hydrocarbon fuel provides the H₂ storage in an open-loop system. Indeed, we face a number of challenging but highly rewarding possibilities through the proposed hybrid hydrogen-carbon economy for a sustainable future.

Methods

Well known process system analysis methods in conjunction with the commercial software ASPEN were used to perform various material and energy balances. The calculation details and results are provided in [supporting information \(SI\) Appendix](#).

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